

tometer and measuring one or more J-coupling parameters using the atomic magnetometer. According to an embodiment, a fluid analyte is polarized in a strong magnetic field (e.g., the Halbach array **108**), which produces the polarized analyte, and then the polarized analyte flows into the detection volume **110** within a zero field region adjacent to the vapor cell **112** of the atomic magnetometer. Pulses can then be applied to prepare a superposition of eigenstates of the J-coupling Hamiltonian, which then evolve freely, without influence of any external field, producing a time dependent magnetization. The magnetic field from the polarized sample is detected by the atomic magnetometer. Advantages of working in a zero field environment include a homogeneous field and temporal stability.

[0028] According to an embodiment of the present invention, the atomic magnetometer works as follows. A single, circularly polarized laser beam optically polarizes orientation in the ground state of the alkali atoms enclosed in the vapor cell **112**. A fully polarized vapor is transparent to the circularly polarized light. A small magnetic field applied to the alkali vapor induces precession of the oriented alkali vapor about the magnetic field, reducing the intensity of the transmitted light which is monitored by the photodiode, thereby producing a measure of the magnetic field. To move away from low frequency noise, a 1.8 kHz modulation of the magnetic field is applied, with amplitude of about 15 nT. This results in modulation of the transmitted light at the second harmonic. An offset in the magnetic field from the J-coupling of the polarized analyte results in a first harmonic, which is detected by the lock-in amplifier. The amplitude of the modulation field is sufficiently small and the oscillation frequency sufficiently fast that their effect on the nuclei to be measured averages to zero. It is emphasized that the single beam embodiment discussed here and shown in FIG. 1 is only one possibility. Other embodiments using two beams to pump and probe either orientation or alignment of the alkali vapor, each with various advantages, are possible. In the implementation depicted in FIG. 1, the magnetometer is sensitive to the z component of the magnetic field. Since the line from the sample to the detection volume lies along the z direction, it is the z component of the magnetization which is detected.

[0029] In the implementation discussed here, polarization of the sample is produced via thermalization in a large magnetic field in a remote location (e.g., the Halbach array **108**). However, other methods of polarization are possible, such as spin-exchange optical pumping, para-hydrogen induced polarization, or dynamic nuclear polarization. Regardless of the prepolarization method, high sensitivity is achieved by the close proximity of the vapor cell **112** to the detection volume **110**.

[0030] According to an embodiment of the present invention, scalar coupling is accomplished as follows. Polarized fluid flows into the detection volume **110** in a zero field environment. A pulse of DC current is applied to one or more of the coils **120**, which applies a magnetic field pulse that rotates spins with different gyromagnetic ratios by different angles about the magnetic field pulse. This places the system in a superposition of eigenstates of the J-coupling Hamiltonian, leading to quantum beats. Evolution due to the J-coupling Hamiltonian produces a modulation of the z component of the magnetization at the quantum beat frequencies, which is then detected by the magnetometer.

[0031] In another embodiment, an additional laser can be employed, yielding approximately a factor of 10 improve-

ment in sensitivity. In this alternative configuration, and with reference to FIG. 1, this second, pump laser is circularly polarized and propagates in the y direction (out of the page). In this embodiment, the pump laser passes through polarizers and a quarter wave plate the same as polarizers **128** and quarter wave plate associated with diode (i.e. probe) laser **116**. The pump laser is tuned to the center of the pressure broadened D1 transition of ^{87}Rb . This polarizes the atoms along the direction of the pump beam propagation. In this arrangement, quarter wave plate **130** is removed from laser **116**, which facilitates tuning of the two lasers, the probe laser now linearly polarized, propagating in the x direction, and tuned two or three pressure broadened line widths off resonance. In the presence of a magnetic field in the z direction, the alkali spins rotate into the x direction. This produces optical rotation of the probe beam. This optical rotation can be detected using a balanced polarimeter consisting of a Wollaston prism (other polarizing beam splitters could work as well) and two photodiodes.

[0032] Operational results for the two laser arrangement are shown at FIG. 6, which in the larger box depicts the sensitivity of the magnetometer as a function of noise vs. frequency. The darker trace shows the actual magnetic field noise of the magnetometer, the lighter trace shows optical noise of the probe beam when the pump beam is blocked. The smaller insert is a plot of optical response vs. frequency, the upper line a plot for in phase responses, the lower line a plot for out of phase responses.

[0033] The use of atomic magnetometers yields greatly improved sensitivity compared to inductive detection at low- or zero-magnetic field because the atomic magnetometers sense magnetic field directly, rather than the time derivative of flux through a pickup coil. Furthermore, in contrast to SQUIDS, atomic magnetometers do not require cryogenics. Examples of the present invention achieved efficient coupling to small samples by making use of millimeter-scale magnetometers (see, V. Shah, S. Knappe, P. D. D. Schwindt, J. Kitching, Subpicotesla atomic magnetometry with a micro-fabricated vapor cell, *Nature Photonics* 1 (2007) 649-652) manufactured using microfabrication techniques (see, S. Knappe et al., Atomic vapour cells for chip-scale atomic clocks with improved long-term frequency stability, *Optics Letters* 30 (2005) 2351-2353). Examples of the present invention employed an 80- μL detection volume. Examples of the present invention also used magnetic shielding, which permits operation in a laboratory environment, where perturbations to the Earth's magnetic field may limit the magnetic field homogeneity and stability.

[0034] Operation at zero field eliminates the chemical shift but retains substantial analytical information in simplified spectra determined by both heteronuclear and homonuclear scalar couplings. The $^{13}\text{CH}_3$ group provides an example of the simplification afforded by spectroscopy in a zero field environment. The Earth's field spectrum consists of eight lines (see, S. Appelt, F. W. Häsing, H. Kuhn, B. Blümich, Phenomena in J-coupled nuclear magnetic resonance spectroscopy in low magnetic fields. *Phys. Rev. A* 76 (2007) 023420), while, as shown here, the zero-field spectrum consists of just two lines, without loss of spectral and analytical information. It is believed that this will facilitate controllable extension into multidimensional spectroscopy with the incorporation of zero-field decoupling and recoupling sequences (see, C. J. Lee, D. Suter, A. Pines, Theory of multiple pulse NMR at low and zero field, *J. Magn. Res.* 75 (1987) 110-124;